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Utilization of distillation residue of 2nd generation bioethanol for fine chemicals production

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Abstract

Distillation residue was waste containing huge amount of water. However, it could not through away to environment due to water pollution. Therefore, some treatments were required. Distillation residue of 2nd generation bioethanol based palm oil empty fruit bunch was hydrothermal liquefied to increase its added value. Process hydrothermal liquefaction was carried out under variation of temperature and reaction time, in an autoclave under inert atmosphere. The product consisted of tar dissolved in water, char and gas. The solid conversion, the tar yields and chemical compounds yields increased by the increasing the reaction temperature. The reaction time did not give significant effect to the conversion and the tar yields (wt %). However, reaction time gave a significant effect to typical chemical compounds in the tar. The typical chemical compounds identified in the tar were acetic acid, phenol, phenol,-2-methoxy and 2-pyrrolidinone. Acetic acid as a fine chemical derived from the distillation residue was recovered as 84% mol after reaction at 325°C for 60 min.

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Keywords: Distillation residue, 2nd generation bioethanol, hydrothermal liquefaction, fine chemicals.

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Nomenclature

C	Celcius
CPO	crude palm oil
DGGS	dried distillers grains with soluble
EFB	empty fruit bunch
g	gram
GC-MS	gas chromatography mass spectroscopy
kg	kilo gram
LHV	low heating value
Min	minutes
MJ	mega joule
wt	weight

1. Introduction

Recently, industrial research has been focused on bioethanol production by utilizing lignocelluloses as raw material that called second generation bioethanol. Several lignocelluloses feedstock were used for bioethanol production such as pinewood, timothy grass, and wheat straw [1]. Other researchers utilized corn, switchgrass, and wood for this purposed [2]. Although many kinds of biomass have potential as feedstock for bioethanol production, the high cost of biomass must be hindrance. In addition on bioethanol production, high yielding energy crops meet a 30% petroleum-based gasoline displacement in 2030. However, the saturation limit of recent research reached 10% blending limit of bioethanol to gasoline [3].

In Indonesia, production of palm oil growth about 10 percent per year [4]. In palm oil plantation, ripe fruit was harvested together with it bunch. The fresh fruit bunch was sent to sterilizer to soften mesocarp using 1.3 bar steam. The fruit was separated from bunch in tracer unit. The fruit was sent to pressing unit for recovery of crude palm oil (CPO) and the bunch was produced as waste that called as empty fruit bunch (EFB). At a conservative estimate, fresh fruit bunch generated 20-21 % of EFB, 11-15% of palm kernels, 20-23% of CPO, 13-23 % of liquid waste and 10-12% of fiber.

The growth of palm oil production automatically will increase in empty fruit bunch (EFB) quantity as agricultural residue. The EFB can be utilized as feedstock for second generation of bioethanol production. During bioethanol production, the EFB as well as lignocelluloses biomass was treated in four stages of pretreatment, hydrolysis, fermentation, and distillation [3]. The bioethanol was produced in the last stage of distillation unit. Beside bioethanol, the distillation unit also produced residue that consisting of water, lignin, non-hydrolyzed and non-fermented organic components, minerals from the feedstock, the added process chemicals and other non-ethanol fermentation products [5]. Distillation residue was waste containing huge amount of water. However, it could not through away to environment due to water pollution. Based on its components, it can be utilized by further processing into valuable materials rather than discharged it to the environment.

There were a few publications in utilization of distillation residue derived from second generation of bioethanol. Maas et al. treated the distillation residue by separation the liquid and solid fractions. The liquid fraction was tested for anaerobic biodegradation yielding biogas (methane) because of its soluble organic components. The average methane content of biogas was 53% per feed. On the other hands, solid fraction was fed into fluidized bed combustor for combined heat and power generation. The lower heating value (LHV) of the solid fraction was 12.4 MJ/kg (dry basis), which is lower than the original wheat straw feedstock (15.6 MJ/kg) because of the increased ash content [5]. Other technology such as hydrothermal liquefaction is also possible to treated the distillation residue. The advantage of the hydrothermal liquefaction was used the residue as intake without liquid and solid separation.

Hydrothermal liquefaction can determined as conversion of biomass into liquid fuels by processing in a pressurized water environment to break down the solid biopolymeric structure to liquid components. Hydrothermal liquefaction usually conducted in range temperatures of 247 – 374 °C. This process aimed to remove oxygen in order the product has higher energy density than raw material [6].

Hydrothermal liquefaction process can be carried out by with and without catalyst. In our previous study, we utilized *dried distillers grains with soluble* (DGGS) by hydrothermal liquefaction and upgraded over iron oxide-based catalyst to produce useful chemical such as ketones [7]. Process of hydrothermal liquefaction that involved catalyst was called as catalytic liquefaction. The catalyst such as alkali was used to modify the ionic medium which can lead to aromatic oil formation. The catalytic liquefaction can be carried out in inert or hydrogen condition [6]. Minowa et al. used sodium carbonate for utilization of forest and agricultural residue to produce biocrude oil with 70% of carbon content and 30 MJ/kg of calorific value [8]. Moreover, Biller and Ross were also used the same catalyst to convert microalgae into biocrude with trend yield of the biocrude as lipid > protein > carbohydrate [9].

In current study, we utilized the distillation residue produced from bioethanol process based empty fruit bunch of palm oil by hydrothermal liquefaction to increase its added value. This process was aimed to produce fine chemicals from the distillation residue under variation of temperature process and reaction time.

2. Experimental

2.1. Composition of distillation residue

Distillation unit of bioethanol pilot plant in Research Center for Chemistry, Indonesian Institute of Sciences was produce bioethanol as distillate and residue as waste. The residue contained huge amount of water. Before used as feed of hydrothermal liquefaction, the residue was precipitated for three days to reduce amount of water. Water at the top layer was removed and sludge in bottom layer of sedimentation unit was used as feed for hydrothermal liquefaction. The sludge hereafter was called as distillation residue and utilized as feed of hydrothermal liquefaction in this study. The distillation residue was analyzed using moisture analyzer (MB45, Ohaus) at 105°C for an hour, HPLC (Waters e2695 Separation Module) and an elemental analyzer (Truespec CHN; Leco) based on ASTM D 5373-08 to identify its composition. The compositions of distillation residue are shown in Table 1. The distillation residue contained 86.92 wt % of moisture. However, such value of moisture content was included ethanol content because of during moisture content analysis, the distillation residue was heated up to 110°C and under this condition ethanol was vaporized together with water. Therefore, total solid content including glucose and xylose in distillation residue was 13.08 wt %.

Table 1. Composition of distillation residue

Component	Concentration [wt. %]
Moisture content	86.92
Ethanol	0.1015
Glucose	0.3757
Xylose	0.0691
Other solid content	12.6352
Elemental analysis	
C	4.08
H	8.84
O	86.18
N	0.90

2.2. Hydrothermal liquefaction

Process hydrothermal liquefaction was carried out in an autoclave made of stainless steel with 280 ml of volume with inside diameter of 5.4 cm. The autoclave was accompanied by a pressure indicator, a thermocouple, a temperature controller, a safety valve, and gas inlet and outlet pipes as shown in Fig. 1. The process was carried out under variation of temperatures as 275-325 °C for 60 min. About 30 g of distillation residue was fed into the autoclave and covered tightly. The autoclave was flushing three times by nitrogen gas, and then heated from room

temperature to liquefaction temperature. Process hydrothermal liquefaction was carried out for 0-90 min after the designed temperatures were reached. Product recovery was conducted after autoclave temperature cooled to room temperature. The product consisted of liquid, solid and gas. The gas product was calculated by subtraction amount of feed with liquid and solid products. The liquid product was analyzed by GC-MS Agilent Technologies 5977A MSD) using n-butanol as internal standard for determination its chemical composition. The GCMS was operated using DB wax column.

As mentioned before, the hydrothermal liquefaction experiments were conducted in an inert atmosphere (purged) with 30 g of distillation residues and produced char, tar dissolve in water and gas. In hydrothermal liquefaction, solid content of distillation residues was decomposed into tar and gas at high temperature and pressure. Its decomposition was called as conversion and calculated according to Equation (1). Tar as a brown aqueous organic material was separated from char by filtration. The composition of the tar consist of heavy component and light component, the heavy components were essentially organics dissolved in water but they were undetectable by gas chromatography because of their high molecular weights [10].

$$\text{Conversion (wt\%)} = \frac{\text{weight of solid content in distillation residues} - \text{weight of char}}{\text{weight of solid content in distillation residues}} \times 100\% \quad (1)$$

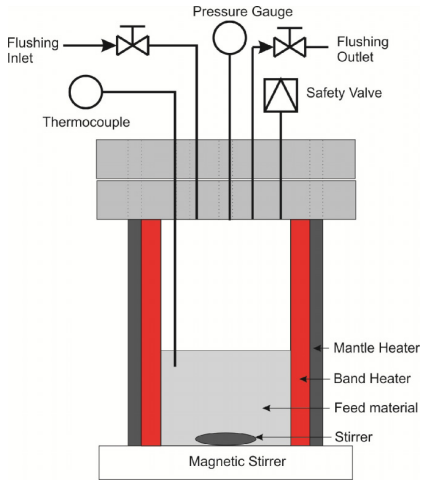

Fig.1. Schematic diagram of an autoclave for hydrothermal liquefaction.

3. Results and Discussion

3.1. Effect of reaction temperature

Figure 2a shows the effect of reaction temperature of hydrothermal treatments on distillation residue's conversion and product yields. The reaction time was fixed for 60 min and the pressure during the reaction varied in a range of 6 - 12.5 MPa depending on reaction temperatures of 275 - 325°C. By increasing the temperature from 275 to 325°C, the conversion increased from 81% to 87% based on solid content of feed, as well as the tar dissolved in water increase from 10.6 wt% to 11.3 wt%. On the other hand, char yields decreased with increasing the reaction temperature. This indicated that an increase in reaction temperature as well as increase in reaction pressure, driving force of reaction medium in liquefaction of distillation residue was increase. Therefore, production of char reduced from 275 – 325°C because char produced from unliquefied distillation residue.

The tar dissolved in water were analyzed using GC-MS and identification of it's the chemical compounds was performed using a NIST mass spectral database. Calculation yield of the chemical compounds in liquid product

based on feed material and presented in % mol as shown in Fig. 2b. The tar contained 2-pyrrolidinone, phenol and acetic acid which is called light component. Meanwhile, the undetectable compounds by GC-MS categorized as heavy component. The major compound identified in the tar was acetic acid that increased from 81% mol to 84% mol by increasing the reaction temperature. Meanwhile, the other two compounds (phenol and 2-pyrrolidinone) slightly increased from 1.3% mol to 2.5% mol and from 1.0% mol to 1.4% mol, respectively. Acetic acid was produced from decomposition of cellulose and 2-pyrrilidinone was produced from nitrogen compound in the feed materials. Meanwhile, phenolic compounds were primarily originated from the degradation of lignin component (by cleavage of the aryl ether linkages in lignin) [11], and also can be derived from cellulose fraction [12].

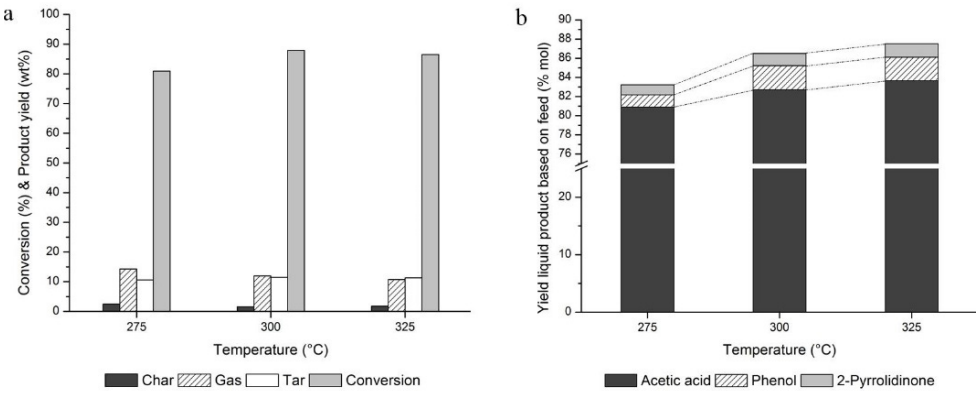

Fig.2. Effect of reaction temperature of hydrothermal liquefaction on distillation residues.

According to Fig. 2a, the conversion of the distillation residue between 300 and 325 °C was almost same. However, yield of liquid product was higher after reaction at 325 °C as shown in Fig. 2b. Therefore, in the next step effect of reaction time was carried out at 325 °C for determination optimum condition.

3.2. Effect of reaction time

In determination the effect of reaction time, hydrothermal liquefaction of distillation residue was carried out for 0, 30, 60 and 90 min at 325°C. Zero min indicated time when the reactor reached a desired temperature (325°C), the heater band was disconnected to electric power and the reactor was cooled down to room temperature using a fan. With an increase in reaction time from 0 to 90 min, conversion was found to slightly increase from 85% to 88% based on solid content of feed, as well as tar dissolved in water yield slightly increase from 87 wt% to 88 wt% respectively (Fig. 3a). On the other hand, the formation of solid products (char) was almost stable in the reaction time ranging from 0 to 90 minutes. It means that the conversion of distillation residue does not strongly dependent on reaction time. However, reaction time gave a significant effect to typical chemical compounds in the tar. There were four compounds identified for 0 min of reaction time, with a new formation of phenol, 2-methoxy compared to previous chemicals (Fig 2b). As shown in Fig. 2b, 0 min of reaction time was produced higher yield of phenol, -2-methoxy, 2-pyrrilidinone and phenol than other holding time of reaction. On the other hand, yield of acetic acid was better after holding time of reaction for 60 min. When the holding time of reaction was longer to 90 min, yields of acetic acid and 2-pyrolidinone were almost unchanged and yield of phenol was slightly increased compared to 60 min. As well as high yield of acetic acid produced from hydrothermal liquefaction, this chemical can be determined as fine chemical derived from the distillation residue. The high yield of acetic acid was produced under 325 °C for 60 min of hydrothermal liquefaction process.

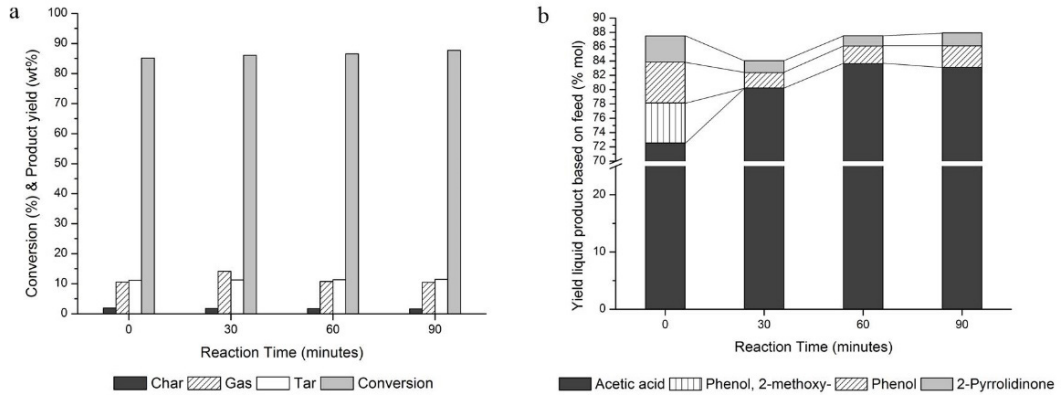

Fig.3. Effect of reaction time of hydrothermal liquefaction on distillation residue

4. Conclusion

Distillation residue of 2nd generation bioethanol based palm oil empty fruit bunch was hydrothermal liquefied under variation of temperature and reaction time. Their thermochemical liquefaction characteristics were systematically compared. The conversion and the tar dissolved in water yields increased by the increasing the temperature reaction form 275 - 325°C. However, the reaction time not so influenced the conversion and the tar yields.

The typical compounds identified in the tar were acetic acid, phenol, 2-pyrrolidinone and phenol,-2-methoxy. Yield of the typical chemical compounds increased as increasing the reaction temperature. The major chemical compound in the tar was acetic acid and the acid was determined as fine chemical derived from the distillation residue through hydrothermal liquefaction process.

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